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(54) Title: REMOVABLE ADHESIVE HAVING HIGH SHEAR AND LOW ADHESIVE TRANSFER

(57) Abstract

A pressure sensitive adhesive comprises: a first component which includes at least one unsaturated vinyl monomer and one emulsifier monomer, a second component which comprises an elastomeric microsphere and a third component which comprises a tacky resin.

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REMOVABLE ADHESIVE HAVING HIGH SHEAR AND
LOW ADHESIVE TRANSFER

FIELD OF THE INVENTION

5 This invention relates to an adhesive which yields high shear and tack values with low adhesion values. More specifically this invention relates to a high shear, high tack, low adhesive transfer, removable adhesive.

10 BACKGROUND OF THE INVENTION

Four properties useful in characterizing the nature of pressure sensitive adhesives are tack, peel strength, shear strength and adhesive transfer. Tack or "quick stick" is the ability of an adhesive to adhere quickly to a surface. Shear strength is the pressure-sensitive adhesive's ability to maintain its position when shearing forces are applied. Peel strength is a measure of the ability of a pressure-sensitive adhesive to resist removal by being peeled away from a surface. Adhesive transfer is the transfer of an adhesive coating to a contact surface such as a painted plaster wall.

Ideally, depending upon the substrate, the adhesive must provide sufficient tack to quickly fix the adhesive to a desired contact surface such as painted drywall wallboard, adequate peel strength to prevent damage of the surface when the adhesive is removed and appropriate cohesive strength to control the transfer of adhesive to the substrate. Balancing these pressure sensitive adhesive properties, particularly in a removable adhesive, poses difficulties to the formulator. For example, some adhesives may permit the removal of a backing from a contact surface to which it had been adhered, but they do not have high shear properties. Other adhesives possess a tack which may be so aggressive as to cause the backing to tear on removal.

U. S. Patent No. 3,922,464 (Silver et al.) discloses a removable adhesive. The Silver et al. adhesive is a stable 35 viscous copolymer latex which includes major amounts of non-tertiary alkyl acrylates, minor amounts of emulsifier monomers, water and if desired, minor amounts of zwitterionic monomers. After these components are mixed, the water is evaporated from the latex leaving a tacky and pressure-sensitive adhesive. The vinyl 40 monomer is selected from the class of non-tertiary alkyl acrylates wherein each alkyl chain has a length of at least 4, but not more than 12 carbon atoms. "Emulsifier monomer," as used herein, is any vinyl-unsaturated, homopolymerizable surfactant which has both a hydrophobic and hydrophilic moiety, contains at least 5, but no

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more than 40 carbon atoms and is non-ionic and/or water dispersible.

As in Silver et al., U.S. Patent No. 4,645,711 (Winslow et al.) also discloses an adhesive comprising a copolymer 5 of alkyl acrylate and a small amount of emulsifier monomer. The Winslow et al. adhesive differs from the Silver et al. adhesive in that it incorporates a tackifier resin.

U.S. Patent No. 4,629,663 (Brown et al.) teaches the use of an adhesive similar to that of Silver et al. The adhesive 10 comprises a terminally unsaturated vinyl monomer and an emulsifier monomer. The adhesive differs from that disclosed in Silver et al. in that the emulsifier monomer is a monovalent salt of styrene sulfonate.

U. S. Patent No. 4,699,842 (Jorgensen et al.) 15 discloses pressure-sensitive adhesives which have balanced adhesive properties over wide temperature ranges. The adhesive composition comprises a first component consisting essentially of a tackified, emulsifiable adhesive and a second component which comprises at least one terminally unsaturated vinyl monomer, at 20 least one vinyl-unsaturated, homopolymerizable, emulsifier monomer and optionally a small amount of an external emulsifier. The second component of Jorgensen et al. can be the adhesive disclosed in either the Silver et al. or the Brown et al. patents.

While the adhesives disclosed in Silver et al., 25 Winslow et al., Brown et al. and Jorgensen et al. demonstrate some degree of removability, there are many applications for adhesives which require a higher degree of removability.

An adhesive having a high degree of removability is disclosed in U.S. Patent Number 3,691,140 (Silver). Silver 30 teaches the use of solid, inherently tacky, acrylate pressure-sensitive adhesive microspheres which when adhered to paper, may be easily removed from the paper surface without delaminating the adhesive or the paper substrate. U. S. Patent No. 4,166,152 (Baker et al.) also teaches the use of solid, inherently tacky 35 methacrylate microspheres prepared from non-ionic alkyl acrylate or methacrylate monomer(s) in the presence of both an emulsifier and an ionic suspension stabilizer having an interfacial tension sufficient to prevent microsphere agglomeration.

In contrast to the solid micropsheres disclosed in 40 Silver and Baker et al., U.S. Patent No. 5,045,569 (Delgado) discloses hollow, inherently tacky pressure sensitive adhesive acrylate microspheres which due to their unique morphology, provide enhanced peel and shear strength and less adhesive transfer to substrates than do solid acrylate microspheres.

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While exhibiting a desirable degree of removability, microsphere adhesives, in some cases, tend to transfer to contact surfaces such as paper. To reduce microsphere transfer, U. S. Patent No. 3,857,731 (Merrill et al.) discloses the use of 5 microspheres embedded in a binder coated on a substrate.

Although having a high degree of removability, the microsphere adhesives in Silver, Baker et al., Delgado, Merrill et al. have less than an optimum amount of shear strength generally rendering them unsuitable for mounting objects such as poster 10 boards.

Thus, there currently exists a need for an adhesive which is easily removed from a contact surface yet offers high shear properties, low peel adhesion and low adhesive transfer values. There also currently exists a need for a removable tape 15 and/or article having these same properties.

SUMMARY OF THE INVENTION

The present invention involves pressure sensitive adhesives which have high shear properties, low peel adhesion and 20 exhibit minimal adhesive transfer. In accordance with this invention, the removable pressure sensitive adhesive comprises a blend of: (a) a first component comprising at least one terminally unsaturated vinyl monomer and at least one vinyl, unsaturated homopolymerizable emulsifier monomer, (b) a second component 25 comprising an infusible, inherently tacky, elastomeric polymeric microsphere and (c) a third component comprising a resin having high adhesion and static shear.

Preferably, the adhesive blend comprises:

(a) from about 40 parts to about 90 parts of a 30 first component comprising from 95 to 99.8 parts by weight of at least one terminally unsaturated vinyl monomer, 60 to 100 weight percent of the monomer being selected from the class of non-tertiary alkyl acrylates wherein each alkyl group has at least half of its carbon atoms in a single chain and the average length 35 of the alkyl chain is at least 4 and not more than 12, and from 0.2 to 5 parts by weight of a least one vinyl-unsaturated homopolymerizable emulsifier monomer which is a surfactant having both a hydrophobic and a hydrophilic moiety, contains at least 5 but no more than 40 carbons atoms and is water-dispersible,

40 (b) from about 3 parts to about 55 parts of a second component comprising infusible, inherently tacky, elastomeric polymeric microspheres and

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(c) from about 5 parts to about 55 parts of a third component consisting essentially of a water-emulsifiable, tacky adhesive.

It is preferred that the second component comprises 5 hollow, infusible, tacky, elastomeric copolymer microspheres.

It is preferred that the third component be a hard resin selected from the group comprising epoxies, nitrocellulose and ethylenes and mixtures thereof.

In another embodiment of the present invention, it is 10 preferred that the third component comprise a soft resin selected from the group consisting of polyolefins, polybutylenes, polyhexenes, polyoctenes, silicones, natural rubbers, acrylates, methacrylates, vinyl acetates and vinyl ethers and mixtures thereof.

15 The novel and unobvious adhesive of the present invention can be applied to one or to both major surfaces of a removable tape and/or article.

DETAILED DESCRIPTION

The invention provides a pressure-sensitive adhesive 20 comprising a blend of three components yielding high shear and tack values with surprisingly low adhesion values.

The first component of the adhesive of the present invention is preferably the copolymer described in U.S. Patent No. 4,629,663 incorporated herein by reference. The copolymer is 25 formed from the monomers consisting essentially of:

(a) from 95 to 99.8 parts by weight of at least one terminally unsaturated vinyl monomer, 60 to 100 weight percent of the vinyl monomer being selected from the class of nontertiary alkyl acrylates wherein each alkyl group has at least half of its 30 carbon atoms in a single chain and the average length of the alkyl chain is at least 4 and not more than 12, and

(b) from 0.2 to 5 parts by weight of at least one unsaturated, homopolymerizable emulsifier monomer which is a surfactant having both a hydrophobic and a hydrophilic moiety, 35 contains at least 5, but not more than 40 carbon atoms and is water dispersable.

The vinyl monomers useful in forming the first component of the present invention are disclosed in Col. 3, line 28 through col. 4, line 2 of U.S. Patent No. 3,922,464 40 incorporated herein by reference. Representative examples of acrylate monomers are isoctyl acrylate and isononyl acrylate. Examples of useful modifying monomers are N-tert-butylacrylamide, N-tert-amylacrylamide, N-isopropylacrylamide, isobutyl acrylate and ethyl acrylate.

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The emulsifier monomer used in making the second component of U.S. Patent No. 3,922,464 comprises a monovalent salt of styrene sulfonate. A monovalent salt of a styrene sulfonate produces substantially coagulum-free latices and polymers 5 produced therefrom tend to have greater hydrolytic stability and latices of higher solids can be obtained which are easier to coat. A substantially coagulum free latex is a latex which neither hangs up on a stirrer nor prematurely plugs up a filter.

Another class of copolymers that can be used as the 10 first component in the present invention is that described in U.S. Patent No. 3,922,464 herein incorporated by reference. The copolymer described in U.S. Patent No. 3,922,464 is formed of monomers consisting essentially of:

(a) from 88 to 99 parts by weight of at least one 15 terminally unsaturated vinyl monomer, 70 to 100 weight percent of said vinyl monomer being selected from the class of non-tertiary alkyl acrylates wherein each alkyl group has at least half of its carbon atoms in a single chain and the average length of the alkyl chain is more than 4 and not more than 12,

20 (b) from 0.2 to 5 parts by weight of at least one vinyl-unsaturated, homopolymerizable emulsifier monomer which is a surfactant having both a hydrophobic and a hydrophilic moiety, contains at least 5 but no more than 40 carbon atoms and is non-ionic and/or water dispersible and

25 (c) from 0 to 10 parts by weight of at least one zwitterion monomer having a radically polymerizable unsaturated group.

Suitable terminally unsaturated vinyl monomers for the second class of copolymers of the second embodiment are set forth 30 in col. 3, line 34 through col. 4, line 2 in U.S. Patent No. 3,922,464. Suitable emulsifier monomers are set forth in col 4, line 12 through line 51 in U.S. Patent No. 3,922,464. Suitable zwitterion monomers are set forth in column 4, line 63 through column 7, line 5 in U.S. Patent No. 3,922,464.

35 The preferred adhesive of the first component differs from the adhesive of U.S. Patent No. 3,922,464, in that the emulsifier monomer comprises a monovalent salt of a styrene sulfonate. In addition, the adhesives in all but one of the examples in U.S. Patent No. 3,922,464 require a zwitterion monomer 40 to provide good adhesion and cohesion.

The second component of the present invention is a microsphere adhesive. Preferably, the microspheres are hollow, polymeric, acrylate, inherently tacky, infusible, solvent insoluble, solvent-dispersible, elastomeric microspheres and

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comprise at least one alkyl acrylate or alkyl methacrylate ester. The hollow microspheres having utility herein are disclosed in detail in U.S. Patent No. 5,045,569 incorporated herein by reference. Such microspheres have one or more interior voids 5 having a diameter of at least about 10 percent of the diameter of the microsphere. The voids typically range in size up to about 100 microns or larger and have diameters from at least 1 to about 250 microns. The hollow preferred microspheres disclosed in U.S. Patent No. 5,045,569 are normally tacky, elastomeric, insoluble 10 but swellable in organic solvents.

Preferably, the hollow microspheres comprise at least 85 parts by weight of at least one alkyl acrylate or one alkyl methacrylate ester and up to 15 parts by weight of at least one polar monomer. The alkyl acrylate or methacrylate monomers useful 15 in preparing the hollow microspheres are those monofunctional unsaturated acrylate or methacrylate esters of non-tertiary alcohols, the alkyl groups which have 4 to about 14 carbon atoms. Such acrylates are oleophobic, water emulsifiable, have restricted water solubility and as homopolymers, generally have glass 20 transition temperatures below about -20°C.

Acrylates useful in forming hollow microspheres are discussed in col. 5, lines 54-68 in U.S. Patent No. 4,994,322. Representative acrylates include isoctyl acrylate, isononyl acrylate, isoamyl acrylate, isodecyl acrylate, 2-ethylhexyl 25 acrylate, n-butyl acrylate and sec-butyl acrylate. Acrylate or methacrylate or other vinyl monomers which, as homopolymers have glass transition temperatures higher than about -20°C, e.g., tert-butyl acrylate, isobornyl acrylate, vinyl acetate, N-vinyl pyrrolidone may be used in conjunction with one or more of the 30 acrylate monomers provided that the glass transition temperature is below about -20°C.

Polar monomers suitable for copolymerization with the acrylate or methacrylate monomers to form hollow microspheres are those which are both somewhat oil-soluble and water soluble. 35 Representative examples of suitable polar monomers include weakly to moderately ionized polar monomers such as acrylic acid, methacrylic acid, itaconic acid, crotalic acid, maleic acid, fumaric acid, sulfoethyl methacrylate and ionic monomers such as sodium methacrylate, ammonium acrylate and ionic monomers such as 40 sodium methacrylate, ammonium acrylate, trimethylamine p-vinyl benzimide, 4,4,9-trimethyl-4-azonia-7-oxo-8-oxa-dec-9-ene-1-sulphonate, N,N-dimethyl-N-(β -methacryloxyethyl) ammonium propionate betaine, trimethylamine methacrylamide, 1,1 dimethyl-1-(2,3-dihydroxypropyl)amine methacrylimide and the like.

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Although the above hollow microspheres are most preferred, the solid, infusible, solvent-dispersible, solvent-insoluble, inherently tacky elastomeric copolymer microspheres disclosed in U.S. Patent No. 3,691,140, incorporated herein by reference are also useful in the present invention. The solid microspheres contain about 90 percent to about 99.5 percent by weight of at least one alkyl acrylate ester and about 0.5 to about 10 percent by weight of at least one monomer selected from the group consisting of substantially oil-insoluble, water-soluble 10 ionic monomers and maleic anhydride. The copolymer microspheres are small in size, having diameters in the range of about 1 to about 250 microns. Preferably, the microspheres have a diameter in the range of between 25 and 50 microns.

The acrylate ester portion of the solid microspheres 15 is oleophobic, water-emulsifiable, substantially water-insoluble and comprises homopolymers which, generally, have glass transition temperatures below about -20°C. Exemplary monomers are iso-octyl acrylate, 4-methyl-2-pentyl acrylate, 2-methyl butyl acrylate and sec-butyl acrylate.

20 The ionic monomer portion of the solid microspheres comprises those monomers which are water-soluble and substantially oil-insoluble, these terms are defined in the aforementioned U.S. Patent No. 3,691,140. Exemplary monomers include trimethylamine methacrylamide, trimethylamine, p-vinyl benzimide, ammonium 25 acrylate, sodium acrylate, N,N-dimethyl-N-1-(2 hydroxypropyl)amine methacrylamide, 4,4,9-trimethyl-4-azonia-7-oxo-8-oxa-dec-9-ene-1-sulphonate, 1,1-dimethyl-1-(2,3-dihydroxypropyl) amine methacrylamide and maleic anhydride.

30 The third component of the present invention is a tacky resin which adds wet grab and mechanical stability to the composition. As used herein "tacky" means having a sticky nature or immediate adhesion on contact with a surface. "High shear" for the third component is defined as a shear higher than that of a microsphere adhesive. The third component should preferably have 35 high adhesion to painted panels, e.g., 99 oz./0.75 inches. (27.5N/1.9cm). Furthermore, it should not exhibit a high rate of adhesive transfer. Suitable third components include hard resins such as epoxies, nitrocellulose and ethylenes and the like having Tg's ranging from about -130 to about -90 °C.

40 In another embodiment of the present invention, the third component can comprise soft resins including any polyolefin, polybutylene, polyhexene, polyoctene, silicone, natural rubber, acrylate, methacrylate, vinyl acetate, vinyl ether and the like having a Tg ranging from about -89 to about +130°C.

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For example, the third component of the present invention can be a resin comprising 5.6 wt. % vinyl acetate, 8.4 % by weight methyl methacrylate and 86.4 5 % by weight 2-ethyl hexyl acrylate sold under trade designation FlexcrysTM 1625 and 5 commercially available from Air Products Company of Allentown, PA. Another suitable third component can be a resin comprising 78.5 % by weight 2-ethylhexyl acrylate, 13.7 % by weight methyl methacrylate, 7.5 % by weight vinyl acetate sold under the trade designation Flexcrys^m 1685 also commercially available from Air 10 Products Company.

A surfactant is typically added to the adhesive to improve mechanical stability of the adhesive. Suitable surfactants include ethylene oxide adducts of 2,4,7,9 tetramethyl-5-decyn-4,7 diol commercially available from companies such as Air 15 Products and Chemicals, Inc. under such trade names as Surfynol^m 420, Surfynol^m 440, Surfynol^m 465 and Surfynol^m 485. In addition, 3,5-dimethyl 1-hexyn-3-ol can be used as a surfactant. This surfactant is sold by Air Products and Chemicals, Inc. under the tradename Surfynol^m 61.

20 The first, second and third components discussed above are mixed together to form the Applicants' adhesive. In general, the adhesive is formulated by sequentially adding the third component to the first. After these two ingredients have been thoroughly mixed, the second component is added. The entire 25 mixing procedure takes from 10 to 30 minutes, but longer mixing times may sometimes be required. Those skilled in the art will recognize that many variations of the above described procedure may be followed.

This novel adhesive comprises from about 40 parts to 30 about 90 parts by weight of the first component, from about 3 parts to about 55 parts by weight of the second component and from about 5 parts to about 55 parts by weight of the third component. Preferably, this adhesive comprises about 65 parts by weight of the first component, about 15 parts by weight of the second 35 component and about 20 parts by weight of the third component.

Applicants' novel adhesive can be used in many ways. Those skilled in the art will recognize that the novel adhesive can be applied to a variety of substrates such as poster boards and tape backings. Substrate, unless otherwise indicated, refers 40 to tape backings as well as any suitable surface to which the adhesive of the present invention may be adhered to. Illustrative examples of the substrates which the pressure-sensitive adhesive can be applied are substrates made of polyesters, polyethylenes, polypropylenes, polyolefins, paper, acetates, polyvinylchloride,

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acrylic, polyvinylidene fluoride, polyvinylchloride acrylates, polyepoxides, polyamides, polyimides, ionomers, alkyds, polyvinyl alcohol esters, styrene polymers, rubber and nylon.

A protective liner can be applied to a coated 5 substrate in order to prevent the backing from adhering to itself prior to use. A protective liner will also protect the adhesive from contamination. The protective release liner is removed prior to use so that the substrate can be applied to a contact surface.

For example, the adhesive can be placed on a tape 10 backing to form a tape. In order to form a pressure-sensitive adhesive tape with the adhesive of the present invention, the adhesive need merely be applied to a suitable backing in any conventional manner. For many purposes, it is preferred that the adhesive be coated on both sides of a tape backing so that the 15 tape can be adhered to two contact surfaces. If desired, the tape can have a protective release liner to prevent the tape from adhering to itself.

Preferred tapes utilizing the adhesive of the present invention have a peel adhesion value high enough to prevent the 20 tape backing from peeling back onto itself, i.e., when the coated backing is adhered to a vertical or horizontal surface, it will not peel back upon itself. Similarly, the static shear value depends upon the amount of adhesive adhered to the backing. The adhesive should generally be able to support the backing. In 25 addition, these tapes should exhibit low adhesive transfer. A tape having an adhesive coating on both major surfaces of a backing should be removable when applied to a contact surface such as a painted panel and while adhered to the contact surface be capable of supporting an object adhered to its second backing 30 surface. The invention will now be more specifically described by the following non-limiting examples, wherein all parts, percentages and ratios are by weight unless otherwise specified.

TESTING

35 A number of tests were performed to characterize the performance of the pressure sensitive adhesive of the present invention.

PEEL ADHESION

40 Peel Adhesion is the force required to remove a coated flexible sheet material from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in ounces (oz.) per 0.75 inches. (N/1.9cm). The procedure followed is:

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First, painted panels are made by spray painting standard 2.5 cm by 7.6 cm glass microscope slides with 3 coats of Glidden Spread Satin Latex Wall Paint #3402 Antique White and are then oven dried for 24 hours at 65.5°C. Upon completion of the 5 painted panels, a strip of tape 0.75 inch (1.90 cm) wide is adhered to the painted panel by rolling a 1.81-kg hard rubber roller twice over the sample tape. Then the adhesive value is measured by attaching the free end of the tape to a scale and moving the painted panel away from the scale at a rate of 12 10 inches per minute (30.5 cm per minute) at an angle of 180°. The resultant force/width in ounces per 0.75 inches (N/1.9cm) is recorded.

In general, the peel adhesion of the adhesive should be sufficient to prevent a substrate to which the adhesive is 15 adhered from peeling back from itself when applied to a contact surface. However, the peel adhesion must be low enough so that damage does not occur to the substrate.

ADHESIVE TRANSFER

20 Adhesive transfer is the transfer of the adhesive to a contact surface. In the examples, adhesive transfer was expressed as the percentage of adhesive transferred to the contact surface. The procedure to determine adhesive transfer is:

25 A 0.75 inch (1.90 cm.) wide tape having both sides of its backing coated with adhesive is applied to the center of an 1 inch wide (2.54 cm) by 9 inch (22.86 cm) long piece of Kromekote paper. The paper and tape are then mounted on a platen. Once on the platen, the test sample is rolled by a 200 gram hard rubber roller. After 30 seconds the tape is peeled and pulled off the 30 paper at an angle of 90° and at a speed of 90 inches per minute (228.6 cm per minute). The paper is then examined for adhesive transfer by optically reviewing an adhesive coated sample and then recording the percentage of adhesive transferred. In general, it is desired that there be less than 0.1% adhesive transfer.

35

STATIC SHEAR

Static Shear is the adhesive's ability to maintain its position when shearing forces are applied. To test static shear, a 0.5 inch by 0.5 inch (1.2 cm by 1.2 cm) portion of a 0.5 inches 40 by 4 inches strip (1.2 cm. by 10.16 cm) of tape is placed on a stainless steel plate. The tape is placed on the plate so that the free end of the tape extends beyond the plate. Once the tape is applied, the plate is positioned 2° from the vertical to prevent peeling and a 500 gram mass is suspended from the tape's

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free end. The test article is then observed for failure. The time required for failure is the measure of the static force.

The static shear value of the adhesive depends upon the substrate to which it is adhered. In the examples, a static 5 shear value of about 50 mins/500 grams or greater was preferred.

PREPARATION OF THE TAPE SAMPLES

Tape samples were prepared by first coating a tape backing with a conventional notch bar coater. The coater was set to provide a dry coating weight of 7 grains/24in². (7 10 grains/154.85 cm²). Once coated, the adhesive was dried for 5 minutes at 65.5°C in an oven. The coated samples were then covered with a piece of release liner to keep the adhesive clean for testing.

15 EXAMPLES

Examples 1-14 and Comparative Examples A-L were carried out to make a comparison between the adhesive of the present invention and adhesives not within the scope of the claimed invention.

20 EXAMPLE 1

A control adhesive example consisting 70 parts of a first component was made of a 87:12:1 mixture of isoctylacrylate, N-tert-octylacrylamide and sodium styrene sulfonate, 20 parts of a 25 second component made of isoctyl acrylate and N-vinyl pyrrolidone and 10 parts of a third component comprising the adhesive sold under the trade name Flexcryl™ 1625.

The sample was prepared by mixing the three components together in the amounts indicated above and stirring moderately 30 for about 10 minutes.

The adhesive was then coated onto a tape backing. The test results are reported in Table 1.

EXAMPLES 2-14

These examples, all of which were prepared utilizing 35 the methods described in Example 1, illustrate various adhesive compositions found within the scope of the present invention. The first component was the adhesive referenced in U.S. Patent No. 4,629,663. The third component was the adhesive sold under the trade name Flexacryl™ 1625. The second component comprised the 40 hollow microspheres referenced in U.S. Patent No. 5,045,569. The ingredients and amounts used to prepare examples of adhesive compositions and test results are set forth in Table 1.

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TABLE 1

Ex.	Wt. % Ratios	Peel Adhesion (oz./0.75 in.)	Adhesive Transfer (%)	Static Force (mins./500 g.)
5	1 70/20/10	8.2	0.000	7875
	2 67/7/26	67.0	0.040	1868
	3 17/62/21	18.1	0.003	452
	4 65/15/20	43.9	0.020	427
	5 40/30/30	10.3	0.050	200
	6 65/30/5	7.0	0.010	17
10	7 56/22/22	9.7	0.030	1266
	8 56/22/22	10.0	0.020	1236
	9 40/55/5	6.3	0.010	3
	10 40/5/55	14.3	0.010	1576
	11 90/5/5	15.6	0.030	10,000+
15	12 56/22/22	7.0	0.020	1921
	13 80/3/17	23.2	0.010	7325
	14 65/5/30	12.2	0.020	1990

Examples 5-12 and 14 were made with a coating of 4 grains/24 in².
 (4 grains/154.85 cm²)

20

COMPARATIVE EXAMPLES

Adhesives in Comparative Examples A-L were made as in Examples 1-14. However, mixtures and ratios of the three components were varied.

25

COMPARATIVE EXAMPLES A-D

Comparative Examples A-D were formulations of adhesive comprising entirely or predominantly the first component. The first component and third components in these comparative examples were made in accordance with Example 1. The second component in Comparative Examples A was made of hollow microspheres as described in U.S. Patent No. 5,045,569. The second component in

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Comparative Example B was made of solid microspheres prepared in accordance with U.S. Patent No. 4,166,152.

The amounts used to prepare these comparative examples and the test results are given in Table 2.

5

TABLE 2

Ex.	Wt. % Ratios	Peel Adhesion (oz./0.75 in.)	Adhesive Transfer (%)	Static Force (mins./ 500 g.)
A	87/13/0	37.4	0.010	5348
B	87/13/0	25.2	0.010	1106
C	70/0/30	31.1	0.003	1038
D	100/0/0	23.9	FAILURE	9869

Upon comparing formulations comprising predominantly or entirely the first component, i.e., Comparative Examples A-D to the properties shown by Examples 1-14, the peel adhesion of the 15 comparative examples, in general, is higher than that shown by the Applicant's adhesive composition. Generally, such peel adhesion rates are undesirable because adhesives having such rates are not good removable adhesives and can possibly damage a substrate to which it is applied.

20

COMPARATIVE EXAMPLES E-H

Comparative Examples E-H were formulations of adhesive comprising entirely or predominantly the second component. The first and second components in these comparative examples were made in accordance with Example 1. The second component in 25 Comparative Example E was made of solid microspheres as described in U.S. Patent No. 4,166,152. The second component in Comparative Example F was made of hollow microspheres as described in U.S. Patent No. 5,045,569. The second component in Comparative Examples G and H was made in accordance with U.S. Patent No. 30 3,857,731. The amounts used to prepare these comparative examples and test results are given in Table 3.

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TABLE 3

Ex.	Wt. % Ratios	Peel Adhesion (oz./0.75 in.)	Adhesive Transfer (%)	Static Force (mins./500 g.)
5	E 0/100/0	10.9	0.090	0.7
	F 0/100/0	3.6	0.010	49.0
	G 0/100/0	NO TEST	46.1	0.0
	H 0/71/29	NO TEST	28.6	0.0

When compared to formulations comprising predominantly the second formulation, i.e., Comparative Examples E-H, the 10 formulations of Applicants' invention have noticeably higher values of static force. The low static forces exhibited by the adhesives of Comparative Examples E-H make them virtually useless for holding objects such as poster boards when adhered to surfaces such as painted plaster walls.

15 COMPARATIVE EXAMPLES I-L

Comparative Examples I-L were formulations of adhesive comprising entirely or predominantly the third component. The first and third components in these comparative examples were made in accordance with Example 1. The second component in Comparative 20 Examples I and K was made of hollow microspheres. Comparative Examples J and L had no second component. The amounts used to prepare these Comparative Examples and test results are reported in Table 4.

TABLE 4

Ex.	Wt. % Ratios	Peel Adhesion (oz./0.75 in.)	Adhesive Transfer (%)	Static Force (mins./500 g.)
25	I 9/4/87	77.5	FAILURE	670
	J 21/0/79	78.9	0.220	1657
	K 0/9/91	76.9	FAILURE	488
	L 0/0/100	99.4	FAILURE	363

30 Applicants' recited formulations as exhibited in Examples 1-14 have lower adhesive transfer values than those shown by

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formulations comprising predominantly or entirely the third component. Comparative Example I-L disclose inordinately high adhesive transfer rates as evidenced by the failure of the Kromekote Paper when it is removed, i.e., the Kromekote Paper tore 5 upon removal. Failure is defined as the cohesive failure of the Kromekote Paper because the adhesion of the adhesive is greater than the cohesive strength of the Kromekote Paper. Such failure is a sign of a high degree of adhesive transfer and demonstrates a low degree of removability.

10 In summary, a novel and unobvious adhesive has been described having unexpected high shear properties, low peel adhesion and little or no adhesive transfer. Although specific embodiments and examples have been disclosed herein, it should be borne in mind that these have been provided by way of explanation 15 and illustration and the present invention is not limited thereby. Certainly modifications which are within the ordinary skill in the art are considered to lie within the scope of this invention as defined by the following claims including all equivalents.

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WE CLAIM:

1. A removable pressure sensitive adhesive comprising:
 - (a) a first component comprising at least one terminally unsaturated vinyl monomer and at least one vinyl, unsaturated homopolymerizable emulsifier monomer,
 - (b) a second component comprising at least one infusible, inherently tacky, elastomeric polymeric microsphere, and
 - 10 (c) a third component comprising a resin having high adhesion and high static shear.
2. The pressure sensitive adhesive of Claim 1 comprising from about 40 parts to about 97 parts of said first component, from about 3 parts to about 55 parts of said second component and from about 5 parts to about 55 parts of said third component.
3. The adhesive of Claim 1 wherein said first component comprises from 95 to 99.8 parts by weight of said terminally unsaturated vinyl monomer, 60 to 100 weight percent of said monomer being selected from the class of non-tertiary alkyl acrylates wherein each alkyl acrylate has at least half of its carbon atoms in a single alkyl chain, the average length of said 25 alkyl chain being at least 4, but not more than 12; and from 0.2 to 5 parts by weight of said vinyl-unsaturated homopolymerizable emulsifier monomer having both a hydrophobic and a hydrophilic moiety, wherein said emulsifier monomer contains at least 5 but not more than 40 carbons atoms.
- 30 4. The adhesive of Claim 1 wherein said first component comprises from 88 to 99 parts by weight of said terminally unsaturated vinyl monomer, 70 to 100 weight percent of said monomer being selected from the class of non-tertiary alkyl acrylates wherein said alkyl acrylate has at least half of its carbon atoms in a single alkyl chain wherein the average length of said alkyl chain is at least 4, but not more than 12; and from 0.2 to 5 parts by weight of a least one vinyl-unsaturated homopolymerizable emulsifier monomer having both a hydrophobic and 35 a hydrophilic moiety, wherein said emulsifier monomer contains at least 5 but no more than 40 carbons atoms and from 0 to 10 parts by weight of at least one zwitterion monomer having a free radically polymerizable unsaturated group.

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5. The adhesive of Claim 1 wherein said third component comprises a hard resin having a glass transition temperatur from about -130° to about -90°C.

5 6. The adhesive of Claim 5 wherein said hard resin is selected from the group comprising epoxies, nitrocelluloses, ethylenes and mixtures thereof.

10 7. The adhesive of Claim 1 wherein said third component comprises a soft resin having a glass transition temperature from about -89° to about +130°C.

15 8. The adhesive of Claim 1 wherein said soft resin is selected from the group comprising polyolefins, polybutylenes, polyhexenes, polyoctenes, silicones, natural rubbers, acrylates, methacrylates, vinyl acetates, vinyl ethers and the mixtures thereof.

20 9. The adhesive of Claim 1 wherein said second component comprises hollow, infusible, tacky elastomeric copolymer microspheres.

25 10. The adhesive of Claim 1 wherein said second component comprises solid, infusible, tacky elastomeric copolymer microspheres.

11. The adhesive of Claim 1 wherein said emulsifier monomer is a monovalent salt of styrene sulfonate.

30 12. The adhesive of Claim 1 further comprising a surfactant.

13. An article comprising a substrate having applied to at least a portion of at least one surface thereof, a coating 35 of a pressure sensitive adhesive comprising:

(a) a first component comprising at least one terminally unsaturated vinyl monomer and at least one vinyl, unsaturated homopolymerizable emulsifier monomer,

40 (b) a second component comprising at least one infusible, inherently tacky, elastomeric polymeric microsphere, and

(c) a third component comprising a resin having high adhesion and high shear.

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14. The article of Claim 13 wherein said adhesive comprises from about 40 parts to about 90 parts of said first component, from about 3 parts to about 55 parts of said second component, and from about 5 parts to about 55 parts of said third component.

15. The article of Claim 13 wherein said first component comprises from 95 to 99.8 parts by weight of said terminally unsaturated vinyl monomer, 60 to 100 weight percent of said monomer being selected from the class of non-tertiary alkyl acrylates wherein each alkyl acrylate has at least half of its carbon atoms in a single alkyl chain, the average length of said alkyl chain being at least 4, but not more than 12; and from 0.2 to 5 parts by weight of said vinyl-unsaturated homopolymerizable emulsifier monomer having both a hydrophobic and a hydrophilic moiety, wherein said emulsifier monomer contains at least 5 but not more than 40 carbons atoms.

16. The article of Claim 13 wherein said first component comprises from 88 to 99 parts by weight of said terminally unsaturated vinyl monomer, 70 to 100 weight percent of said monomer being selected from the class of non-tertiary alkyl acrylates wherein said alkyl acrylate has at least half of its carbon atoms in a single alkyl chain wherein the average length of said alkyl chain is at least 4, but not more than 12; and from 0.2 to 5 parts by weight of a least one vinyl-unsaturated homopolymerizable emulsifier monomer having both a hydrophobic and a hydrophilic moiety, wherein said emulsifier monomer contains at least 5 but no more than 40 carbons atoms and from 0 to 10 parts by weight of at least one zwitterion monomer having a free radically polymerizable unsaturated group.

17. The article of Claim 13 wherein said third component comprises a hard resin having a glass transition temperature from about -130° to about -90°C.

18. The article of Claim 16 wherein said hard resin is selected from the group comprising epoxies, nitrocellulose and ethylenes and mixtures thereof.

19. The article of Claim 13 wherein said third component comprises a soft resin having a glass transition temperature from about -89° to about +130°C.

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20. The article of Claim 19 wherein said soft resin is selected from the group comprising polyolefins, polybutylenes, polyhexenes, polyoctenes, silicones, natural rubbers, acrylates, methacrylates, vinyl acetates, vinyl ethers and the mixtures 5 thereof.

21. The article of Claim 13 wherein said second component comprises hollow, infusible, tacky elastomeric copolymer microspheres.

10 22. The article of Claim 13 wherein said second component comprise a solid, infusible, tacky elastomeric copolymer microspheres.

15 23. The article of Claim 13 wherein said emulsifier monomer is a monovalent salt of styrene sulfonate.

24. The article of Claim 13 further comprising a surfactant added to said adhesive composition.

20 25. The article of Claim 13 further comprising a protective release liner applied to said coated portion of said substrate.

25

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/00192

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 C09J4/06

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1. 5	C09J

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passage ¹²	Relevant to Claim No ¹³
Y	EP,A,0 180 434 (MINNESOTA MINING AND MANUFACTURING COMPANY) 7 May 1986 cited in the application see claims 1-8 & US,A,4 629 663 ----	1-25
Y	FR,A,2 224 536 (MINNESOTA MINING AND MANUFACTURING COMPANY) 31 October 1974 cited in the application see page 5, line 17 - line 28 & US,A,3 857 731 ----	1-25
A	FR,A,2 189 489 (MINNESOTA MINING AND MANUFACTURING COMPANY) 25 January 1974 cited in the application & US,A,3 922 464 ----	1,4,13, 16 -/-

¹⁰ Special categories of cited documents :¹⁰

- ^{"A"} document defining the general state of the art which is not considered to be of particular relevance
- ^{"E"} earlier document but published on or after the international filing date
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- ^{"O"} document referring to an oral disclosure, use, exhibition or other means
- ^{"P"} document published prior to the international filing date but later than the priority date claimed

- ^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- ^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- ^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- ^{"A"} document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

21 APRIL 1993

Date of Mailing of this International Search Report

10.05.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

ANDRIOLLO G.R.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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A	EP,A,0 044 359 (INTERNATIONAL COATINGS) 27 January 1982 -----	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9300192
SA 69041

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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